

# PATENT SPECIFICATION

**L.153,196**



NO DRAWINGS

**L.153,196**

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No. 25567/66.

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(Patent of Addition to No. 1,026,978 dated 12 March, 1963.)

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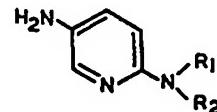
Index at acceptance:—D1 B2A1

Int. Cl.:—D 06 p 3/08

## COMPLETE SPECIFICATION

### Method of Dyeing Hair

- We, SCHWARZKOPF VERWALTUNG G.M.B.H.,  
a body corporate and existing under the laws  
of Germany, of Hohenzollernring 127—129,  
Hamburg-Altona, Germany, trading as HANS  
5 SCHWARZKOPF, do hereby declare the invention,  
for which we pray that a patent may be  
granted to us, and the method by which it is  
to be performed, to be particularly described  
in and by the following statement:—
- 10 This invention relates to oxidation hair  
dyes, i.e. hair dyes which are applied to the  
hair and oxidised *in situ* to develop the dye  
colour.
- In our U.K. patent specification No.  
15 1,026,978 there is disclosed and claimed a  
method of dyeing hair in which the hair is  
treated with a neutral or slightly alkaline com-  
position containing 2,5-diaminopyridine. After  
application the dye is developed by oxidation,  
20 for example, by means of hydrogen peroxide.  
By this method a good red colour can be  
obtained which is highly resistant to moisture.
- In accordance with the present invention it  
has been found that equally satisfactory results  
25 can be obtained using 2,5-diaminopyridines  
substituted in the 2-amino group. In particular  
the dyes according to the present invention are  
excellent for obtaining red and orange nuances  
in the hair which have a high resistance to  
washing, light and diffusion, are uniform in the  
30 colours obtained and are stable over a wide  
pH range. These dyes are therefore markedly  
superior to the previously used nitro com-  
pounds.
- 35 The substituted 2,5-diaminopyridines used  
in this invention are of the formula



where R<sub>1</sub> represents hydrogen or an alkyl,  
cycloalkyl, hydroxyalkyl, amino-  
alkyl, alkoxyalkyl or aryl group;

40 and

R<sub>2</sub> represents an alkyl, cycloalkyl,  
hydroxyalkyl, aminoalkyl, dialkyl-  
aminoalkyl, aralkylalkoxyalkyl aryl  
or aminopyridyl group.

45

Typical substituents on the 2-amino nitrogen  
include methyl, hydroxyethyl, cyclohexyl,  
methoxypropyl, dimethylaminopropyl, benzyl  
and phenyl. These derivatives may be used  
either alone, combined with one another or  
combined with known benzenoid oxidation dyes  
or pyridine oxidation dyes.

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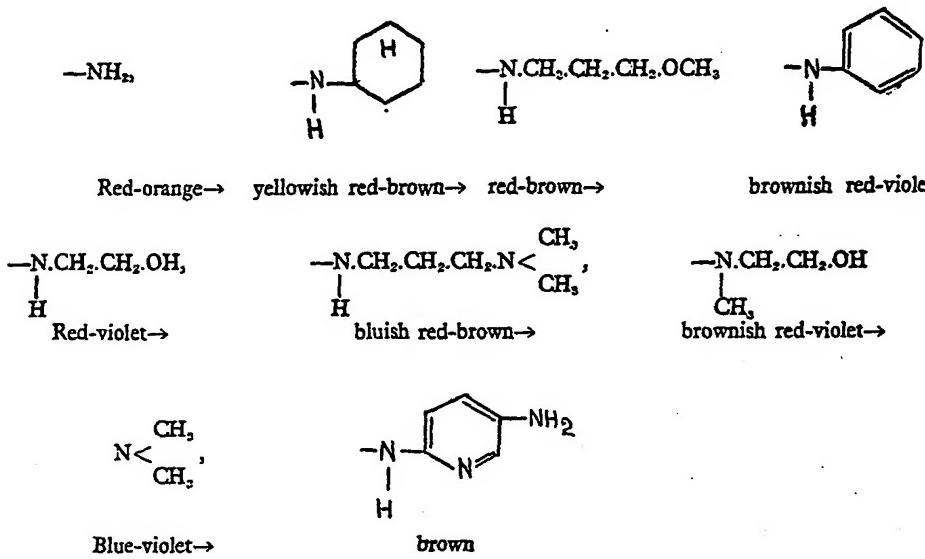
In contrast to unsubstituted 2,5-diaminopyr-  
idine, which can be used to provide only a red  
tint, the use of the substituted derivatives in  
accordance with this invention opens up quite  
new nuances for genuine tinting. In general  
the following rule can be postulated concerning  
the influence of substituents in the 2-amino  
group of 2,5-diaminopyridine:

55

The colouring effect increases from orange  
through red to blue-violet in the following  
order of substituents:

60

[Price 4s. 6d.]



- 5 The preparation of the compounds used in this invention takes place by known methods and does not form part of the invention. For example, the 2-alkylamino-5-aminopyridine compounds may be formed by reacting 2,5-diaminopyridine with alkyl halides, alkyl sulphates or diazomethane or by the method of Tschitschibabin in the presence of sodium amide. 2-Dimethylamino-5-aminopyridine can be obtained in good yield by reacting 2-amino-5-nitropyridine with methyl iodide in the presence of sodium amide and then reducing the resultant compound, similar to the method of Tschitschibabin and Knunjanz.
- 10 As in the parent case, the dye compound is applied to the hair in a neutral or slightly alkaline medium, preferably an ammoniacal medium, and may be a solution, cream or paste. After application the dye compound, which is colourless, is developed by oxidation to give the desired colour. This oxidation may result simply from atmospheric oxygen in which case rather lighter shades develop, or oxidation may be effected by using a chemical oxidant, usually hydrogen peroxide, which may be applied to the hair separately or it may be mixed with the dye composition immediately before application. The latter oxidation method results in deeper fashionable hair shades.
- 15 In addition to the dye compound, the com-

positions will generally contain conventional additives such as thickeners, stabilisers or emulsifiers. In the Examples which follow such additives are not included for the sake of simplicity. 35

#### EXAMPLE 1. 40

A solution is made up from:

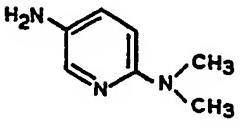
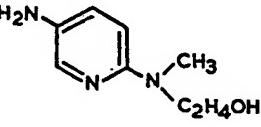
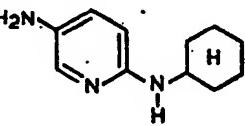
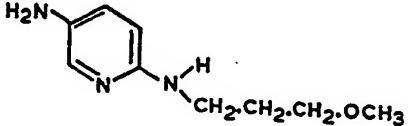
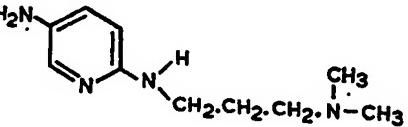
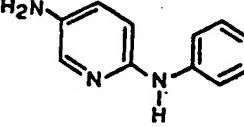
2.0 g. 2 - hydroxyethylamino - 5 - amino-pyridine - hydrochloride  
4.0 g. 25% ammonia and  
94.0 g. water. 45

The solution is applied to bleached hair, left to act for 30 minutes during which time atmospheric oxidation takes place. The hair is then rinsed and dried. The result is a beautiful purple shade with good resistance to wetting. 50

#### EXAMPLE 2. 55

70 g. of the solution from Example 1 is mixed with 30 ml 6% hydrogen peroxide and the mixture is allowed to act on the hair. After a dyeing time of 20 minutes at room temperature the hair is rinsed. An extremely deep stable purple is obtained. 60

The following table summarises the dyeing performance of other derivatives of 2,5-diaminopyridine using compositions and dyeing procedures similar to those described in Examples 1 and 2.

Example No.	Formula		
3		2-dimethylamino-5-amino-pyridine	blue-violet
4		2-(N-methyl-N-hydroxyethyl)amino-5-aminopyridine	brownish red-violet
5		2-cyclohexylamino-5-aminopyridine	yellowish red-brown
6		2-(γ-methoxypropyl)-amino-5-aminopyridine	red-brown
7		2-(γ-dimethylaminopropyl)amino-5-aminopyridine	Bluish red-brown
8		2-phenylamino-5-aminopyridine	brownish red-violet

**EXAMPLE 9.**

A solution is made up from:

- 2.0 g. 2 - dimethylamino - 5 - aminopyridine;  
 5 1.0 g. 2 - methyl - hydroxyethylamino - 5 - aminopyridine.  
 4.0 g. 25% ammonia  
 93 g. water.

After application and developing as in example 10 the hair takes on a quiet violet shade. Developed as in example 2 (with  $H_2O_2$ ) a deep bordeaux red tint is obtained.

**EXAMPLE 10.**  
A solution is made up from:

- 15 1.0 g. p-toluylenediamine sulphate  
 1.0 g. 2 - methyl - hydroxyethylamino - 5 - aminopyridine  
 94.0 g. water.  
 4.0 g. 25% ammonia

20 The solution is applied to hair and developed as in example 2. The hair is dyed a light chestnut shade.

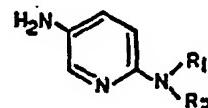
**EXAMPLE 11.**  
A solution is made up from:

- 25 2.0 g. 2 - hydroxyethyl amino - 5 - aminopyridine - hydrochloride  
 0.1 g. 2,6-diaminopyridine  
 93.9 g. water.  
 4.0 g. 25% ammonia

30 The solution is used as in Example 2, to produce a very natural looking ash blonde tint. In this case the 2,6-diaminopyridine has acted as a modifier.

**WHAT WE CLAIM IS:—**

- 35 1. A method of dyeing hair in which the hair is treated with a neutral or slightly alkaline composition containing one or more substituted 2,5-diaminopyridines of the formula:



where  $R_1$  represents hydrogen or an alkyl, cycloalkyl, hydroxyalkyl, aminoalkyl, alkoxyalkyl or aryl group, and  $R_2$  represents an alkyl, cycloalkyl, hydroxyalkyl, aminoalkyl, dialkylaminoalkyl, aralkyl, alkoxyalkyl, aryl or amino-pyridyl group, followed by oxidation to develop the dye. 40

2. A method according to claim 1, in which the said pyridine derivative is 2 - dimethylamino - 5 - aminopyridine, 2 - (N - methyl-N - hydroxyethyl)amino - 5 - aminopyridine, 2 - cyclohexylamino - 5 - aminopyridine, 2 - ( $\gamma$  - methoxypropyl)amino - 5 - aminopyridine, 2 - ( $\gamma$  - dimethylaminopropyl)amino - 5 - aminopyridine or 2 - phenylamino - 5 - aminopyridine. 45

3. A method according to claim 1, in which the composition also contains a benzenoid or pyridine compound known as an oxidation hair dye. 50

4. A method according to any one of the preceding claims, in which the composition is an ammoniacal solution, cream or paste. 55

5. A method according to any one of the preceding claims, in which the dye is developed by means of a chemical oxidant other than atmospheric oxygen. 60

6. A method according to claim 5, in which the oxidant is hydrogen peroxide. 65

7. A method according to claim 5 or 6, in which the oxidant is mixed with the dye composition immediately prior to application to the hair. 70

8. A method according to claim 1, substantially as described in any one of the foregoing Examples. 75

9. Hair when dyed by a method claimed in any one of the preceding claims.

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